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Short communication

Estimation of liquid viscosity at ambient temperature of pure organic compounds by using group-interaction contributions

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Abstract

A new method is proposed to estimate the liquid viscosities at ambient temperature (20°C) of pure organic compounds from chemical structure. Estimation is performed by using a new structural approach (GIG), which considers the contributions of interactions between bonding groups in the molecule instead of the contributions of simple groups. Compared to other group-contribution methods, the proposed method demonstrates significant improvements in accuracy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Viscosity prediction; Group-contribution methods; Isomers; Group-interaction contribution

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1. Introduction

In the chemical industry, liquid viscosity is an important property in hydraulics calculations for surface facilities, pipeline systems and flow through porous media. With the increased popularity of process and reservoir simulators, there is an increasing need for consistent, reliable and accurate predictive methods for liquid viscosity calculations.

Gas phase viscosity is primarily a function of momentum transfer by translation of the molecules with relatively few collisions and has been rather well described by kinetic theory of gases. In liquids, however, the momentum transfer is dominated by collisions and interacting force fields between the densely packed molecules. Therefore, the theoretical description of liquid phase viscosity is difficult due to these intermolecular forces. In spite of the tremendous efforts aimed at including these effects in models, there is no widely accepted theoretical method to calculate viscosity of pure liquids [1].

Numerous empirical methods have been proposed to calculate liquid viscosity on an intuitive basis due to the complexity of the theoretical approach [2–6]. These methods are based on empirical equations that correlate viscosity with chemical structure and/or some other properties. Although these methods have had some moderate success, most of them yield large errors even for simple organic compounds or require input properties that are not currently available or need to be previously estimated. Besides, the relationship between chemical structure and viscosity is performed by using group-contribution techniques, which do not represent satisfactorily the effects of intermolecular forces because of their very simplified representation of chemical structure.

To overcome some of the limitations of the preceding techniques, Pardillo-Fontdevila and González-Rubio [7] have proposed a new structural approach (GIC), which considers the contributions of interactions between bonding groups instead of the contributions of simple groups. Recently, Marrero-Morejón and Pardillo-Fontdevila [8] developed a new method based on GIC for the estimation of critical constants and normal boiling temperatures of organic compounds. In this work, we propose a new method, also based on this new approach, for the estimation of liquid viscosity at ambient temperature (20°C) of pure organic compounds.

2. Development of the method

In this work, the viscosity of a pure organic liquid is considered to be a function of a structurally dependent parameter (Σ), which is thereby determined by summing the number frequency of each group-interaction occurring in the molecule times its contribution. We selected 35 simple

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Table 1
Contributions of group-interactions (non-ring groups)[a]

	–CH$_3$	–CH$_2$	>CH–	>C<	(=)CH–	(–)CH=	(=)C<	(–)–C=	–F	–Cl	–Br	–I	–OH(a)	–O–	>CO	–CHO
–CH$_3$	0.4712 (1)	0.2588 (105)	0.2472 (34)	0.1833 (8)		0.0834 (1)		0.1670 (4)		0.6294 (1)	0.7161 (1)	0.6086 (1)	2.6902 (1)	0.4020 (2)	0.5475 (7)	1.3881 (1)
–CH$_2$–		0.0973 (75)	−0.0543 (28)	−0.0417 (6)		−0.0775 (11)		−0.0488 (1)		0.7214 (10)	0.5799 (4)	0.3971 (2)	2.9295 (17)	0.1089 (10)	0.2605 (6)	1.0415 (3)
> CH–			−0.1470 (3)	0.1181 (3)						0.3633 (7)	0.6838 (2)		2.9212 (2)	−0.1711 (1)	0.2242 (1)	
>C<									−0.1491 (2)	0.2947 (1)			2.8610 (1)			
=CH$_2$					0.2894 (14)		0.3306 (4)									
(=)CH–					0.3096 (5)		0.1060 (1)									
(–)CH=								−0.0465 (1)		0.3593 (2)				−0.0982 (1)		1.1338 (1)
(=)C<							0.2482 (1)									
(–)–C=										0.1831 (2)						
–F																
–Cl																
–Br															0.0726 (1)	

	–COOH	(–)COO–	(–)OOC–	–H	–NH$_2$	>NH	>N–	–CN	–NO$_2$	–SH	–S–	>CH–[*]	=C–(–)[*]
–CH$_3$	2.6110 (1)	0.5904 (8)	0.6410 (6)			1.3476 (2)	0.1695 (2)	1.9082 (1)	1.9476 (1)		0.5587 (1)	−0.0926 (3)	0.0314 (17)
–CH$_2$–	1.9798 (2)	0.2089 (7)	0.3632 (18)		1.5471 (3)	0.2857 (3)	−0.0047 (3)	1.3879 (3)	1.4679 (1)	0.7255 (2)	0.2785 (1)	−0.4464 (2)	−0.4327 (5)
>CH–	1.6883 (1)	−0.0606 (1)											−0.0701 (3)
>C<	1.9524 (1)												
=CH$_2$													
(=)CH–													
(–)CH=		1.1345 (1)	0.1966 (1)					1.2214 (1)					−0.2144 (2)
(=)C<													
(–)–C=	1.7215 (1)							0.8265 (1)					
–F													−0.1932 (4)
–Cl													0.0404 (3)
–Br													−0.0847 (2)
–I													0.0139 (1)
–OH(a)												4.3481 (1)	
–OH(p)													3.1712 (1)
–O–													0.0963 (2)
>CO						1.8611 (1)	1.8010 (1)						0.2243 (2)
–CHO													0.7089 (1)
(–)COO–				0.6194 (4)									0.1514 (4)
–NH$_2$												0.6492 (1)	1.7430 (4)
>NH													−0.1640 (1)
>N–													0.1721 (2)
–NO$_2$													0.8012 (3)
–SH													0.5036 (1)

[a] Blank spaces correspond to unfeasible interactions or contributions that could not be determined; (–) indicates interactions occurring via single bond; (=) indicates interactions occurring via double bond; [*] indicates a ring group interacting with a non-ring group.

Table 2
Contributions of group-inteactions (ring groups)[a]

	–CH$_2$–	>CH–	>C<	(=)CH–	(–)CH=	(=)C<	(–)–C=
–CH$_2$–	0.2980 (19)						
>CH–	0.2136 (8)	−0.3205 (2)					
>C<	0.1692 (1)						
(=)CH–				0.0952 (53)			
(–)CH=	0.2675 (2)				0.3422 (52)		
(=)C<				0.2486 (41)		0.4700 (9)	
(–)–C=	−0.0704 (1)				0.2130 (49)		0.2292 (2)
–O–	0.3781 (5)	0.8726 (2)			0.3708 (1)		
>CO	0.6534 (2)						
>NH	0.6341 (2)				1.0147 (1)		
>N–							
(=)N–				0.5734 (1)		0.7030 (1)	
(–)N=					0.5751 (1)		0.1880 (1)
–S–	0.5436 (1)				0.5128 (1)		

[a] Blank spaces correspond to unfeasible interactions or contributions that could no be determined; (–) indicates interactions occurring via single bond; (=) indicates interactions occurring via double bond.

groups to generate a consistent set of group-interactions that allows one to treat a wide variety of organic compounds. These groups are the same as used by Joback and Reid [5], with the omission of non-ring groups =C=, ≡CH, ≡C–, =NH and =N–.

A representative set of 230 pure organic compounds was employed in the development of the proposed method. The experimental liquid viscosity data at 20°C and normal pressure were obtained from an excellent compilation reported by Suzuki et al. [6] and range 0.197–128.0 mPa s. A least-square optimization has been carried out to determine the contributions of group-interactions. The method is expressed by the following equation:

$$\ln(\eta_L) = 1.279\,M + \Sigma - 7.6425 \quad \{\text{or } \eta_L = M^{1.279}\exp(\Sigma - 7.6425)\} \qquad (1)$$

$$n = 230, \quad r^2 = 0.957, \quad \text{std} = 2.474$$

where η_L and M denote liquid viscosity (mPa s) at 20°C and the molecular weight (g/mol), respectively. Here, the average relative error, $\Sigma[\{|\eta(\text{obsv}) - \eta(\text{calc})|/\eta(\text{obsv})\} \times 100]/230$, is 8.7%. The contributions of group-interactions are listed in Tables 1 and 2 together with the number of compounds used to calculate each contribution value. Notice that some group-interactions have not been calculated because of the lack of viscosity values of the compounds involving these interactions. The optimization algorithm used for linear regression was Singular Value Decomposition procedure [9]. The objective function was to minimize the sum of squares of the absolute differences between experimental and calculated values.

3. Reliability of the method

In order to test the reliability of the models, we have generated two disjointed subsets by randomly excluding 30 compounds from the entire data set of 230 compounds. The remaining compounds have been used as a training set for fitting the proposed equation and determining the contributions of group-interactions. The excluded compounds were used as a testing set by calculating their liquid viscosity values through the contributions and fitted equation previously obtained using the training set compounds. The average relative error for the testing set compounds is 12.7%, which is comparable with those for the training set's compounds, 8.9%. Since the presented method seems to perform well for compounds not included in the training set, it is more suitable to employ the contributions calculated by using the entire data set, which are reported in Tables 1 and 2, because of its larger size.

4. Examples and discussion

To illustrate our proposed application of the GIC approach, we have estimated the value of liquid viscosity using

Table 3
Summation of group-interaction contributions for dibutyl *o*-phthalate

Interactions in the ring	No.	Contributions	
(=)CH– and (=)CH–	2	0.0952	0.1904
(–)CH= and (–)CH=	1	0.3422	0.3422
(–)CH= and (–)–C=	2	0.2130	0.4260
(=)C< and (=)C<	1	0.4700	0.4700
(–)–C= and (–)COO–	2	0.1514	0.3028
Interactions in aliphatic chains			
–CH$_2$– and (–)OOC–	2	0.3632	0.7264
–CH$_2$– and –CH$_2$–	4	0.0975	0.3900
–CH$_2$– and –CH$_3$	2	0.2588	0.5176
Summation for structural parameter (Σ)			3.3654
Estimated value from Eq. (1)			18.58 cP
Experimental value from Suzuki et al. [6]			19.91 cP
Relative error			6.7%

Table 4
Comparison of viscosity estimation methods

	Relative absolute error (%)
Thomas [2]	30.8
Orrick and Erbar [4]	19.9
van Velzen et al. [3]	19.1
Joback and Reid [5]	16.8
Suzuki et al. [6]	17.7
Proposed method	8.9

dibutyl *o*-phthalate as example compound. In Table 3, we show the group-interaction contribution summation using the values from Tables 1 and 2.

The proposed method was found to be quite satisfactory for the most of chemical classes (alkanes, alkenes, cycloalkanes, cycloalkenes, aromatic hydrocarbons, ethers, aldehydes, ketones, acids, esters as well as nitrogen, sulfur and halogenated compounds), and relatively poor for alcohols, phenols and large heterocyclic compounds. Large errors are yielded for polyhydroxy alcohols. In Table 4, we present a comparison between the proposed method and those of Thomas [2], vanVelzen et al. [3], Orrick and Erbar [4], Joback and Reid [5] and Suzuki et al. [6] by using a sample of 50 non-polar and polar compounds. The proposed method yielded the least error. In order to obtain approximate viscosities at other temperatures, the well-known chart proposed by Lewis and Squires [10] can be used.

5. Conclusion

A new method for the estimation of viscosity at ambient temperature of pure organic compound has been developed by using the group-interaction contribution approach (GIG). Compared to other methods, the proposed one exhibits a superior accuracy. Motivated by this result, we are currently extended the method for the estimation of liquid viscosity at other temperatures.

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References

[1] W.D. Monnery, W.Y. Svrcek, A.K. Mehrotra, Viscosity: a critical review of practical predictive and correlative methods, Can. J. Chem. Eng. 73 (1995) 3–50.
[2] L.H. Thomas, The dependence of the viscosities of liquids on reduced temperature, and a relation between viscosity, density and chemical constitution, J. Chem. Soc. 1946 (1946) 573–579.
[3] D. van Velzen, R.L. Cardozo, H. Langenkamp, A liquid viscosity-temperature-chemical constitution relation for organic compounds, Ind. Eng. Chem. Fundam. 11 (1972) 20–25.
[4] C. Orrick, J.H. Erbar, Private communication (1974), in: R.C. Reid, J.M. Praunitz, B.E. Poling (Eds.), The Properties of Gases and Liquids, McGraw-Hill, New York, 1977.
[5] K.G. Joback, R.C. Reid, Estimation of pure-component properties from group-contributions, Chem. Eng. Commun. 57 (1987) 233–243.
[6] T. Suzuki, K. Ohtaguchi, K. Koide, Computer-assisted approach to develop a new prediction method of liquid viscosity of organic compounds, Computers Chem. Eng. 20 (1996) 161–173.
[7] E. Pardillo-Fontdevila, R. González-Rubio, A group-interaction contribution approach. A new strategy for the estimation of physico-chemical properties of branched isomers, Chem. Eng. Commun. 163 (1997) 245–254.
[8] J. Marrero-Morejón, E. Pardillo-Fontdevila, Estimation of pure compound properties using group-interaction contributions, AIChEJ. 45 (1999) 615–621.
[9] G.E. Forsythe, M.A. Malcolm, C.B. Moler, Computer Methods for Mathematical Computations, Prentice-Hall, Englewood Cliffs, NJ, 1977.
[10] W.K. Lewis, L. Squires, The structure of liquids and the mechanism of viscosity, Refiner Nat. Gasoline Manuf. 13 (1934) 448.